

**What is claimed is:**

**[Claim 1]** A method of forming and detecting a mark on a substrate comprising:  
applying a marking material to the substrate to form a mark that reflects or absorbs radiation at a predetermined wavelength within the range of from about 0.75  $\mu\text{m}$  to about 40  $\mu\text{m}$  at a sufficiently different level than the substrate adjacent to the mark such that the mark can be discerned from the substrate at the predetermined wavelength;  
applying a cover coating material comprising an inorganic pigment over the mark and over at least a portion of the substrate adjacent to the mark to form a cover coat that appears substantially opaque in the visible portion of the electromagnetic spectrum but is sufficiently transmissive of radiation emitted at the predetermined wavelength that the mark can be discerned from the substrate through the cover coat at the predetermined wavelength; and  
detecting the mark applied to the substrate using an infrared detecting device.

**[Claim 2]** The method according to claim 1 wherein the substrate is a surface of a part for installation in a land vehicle or aircraft.

**[Claim 3]** The method according to claim 1 wherein the substrate is a primer coat layer applied to a surface of an article.

**[Claim 4]** The method according to claim 1 wherein the marking material comprises an infrared reflective inorganic pigment.

**[Claim 5]** The method according to claim 4 wherein the infrared reflective inorganic pigment is one or more selected from the group consisting of:

$\text{Mn}_2\text{V}_2\text{O}_7$ ;

$\text{M1}_x\text{MnO}_y$ , where M1 is calcium, strontium, barium, magnesium, yttrium and/or an element selected from the Lanthanide series of the Periodic Table of the Elements, x is a number from about 0.01 to about 99, and y is greater than or equal to  $X + 1$  and less than or equal to  $X + 2$  and designates the number of oxygen atoms required to maintain electroneutrality;

$\text{Bi}_2\text{Mn}_4\text{O}_{10}$ ; and

solid solutions having a corundum-hematite crystalline structure comprising iron oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, chrome, cobalt, gallium, indium, lanthanum, lithium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc; and

solid solutions having a corundum-hematite crystalline structure comprising chrome oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, cobalt, gallium, indium, iron, lanthanum, lithium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc.

**[Claim 6]** The method according to claim 1 wherein the average particle size of the inorganic pigment in the cover coating material is from about 0.02 µm to about 15 µm.

**[Claim 7]** The method according to claim 1 wherein the average particle size of the inorganic pigment in the cover coating material is from about 0.1 µm to about 0.5 µm.

**[Claim 8]** The method according to claim 1 wherein the substrate is selected from the group consisting of metal, glass, wood, paper, plastic and ceramic.

**[Claim 9]** The method according to claim 1 wherein the marking material is selected from the group consisting of paint, enamel, laser marking composition, glass, ink, putties and fillers, chemical etchants and transfer films.

**[Claim 10]** The method according to claim 1 wherein the cover coating material is selected from the group consisting of paint, glass, enamel, ink, and transfer films.

**[Claim 11]** The method according to claim 1 wherein the mark is in the form of a machine-readable code.

**[Claim 12]** The method according to claim 1 wherein the inorganic pigment in the cover coating material is doped with one or more elements such that the inorganic pigment provides a uniquely identifiable spectral curve.

**[Claim 13]** The method according to claim 1 wherein the cover coating material comprises two or more different inorganic pigments that together provide a uniquely identifiable spectral curve.

**[Claim 14]** A method of forming a durable infrared detectable mark on a substrate comprising:

applying a marking material to the substrate to form a mark;

applying a contrast marking material to the substrate to form a contrast mark proximal to the mark, wherein the mark reflects or absorbs radiation at a predetermined wavelength within the range of from about 0.75 µm to about 40 µm at a sufficiently different level than the contrast mark such that the mark can be discerned from the contrast mark at the predetermined wavelength; and applying a cover coating material comprising an inorganic pigment over the mark and the contrast mark to form a cover coat that appears substantially opaque in the

visible portion of the electromagnetic spectrum but is sufficiently transmissive of radiation emitted at the predetermined wavelength that the mark can be discerned from the contrast mark through the cover coat at the predetermined wavelength.

**[Claim 15]** The method according to claim 14 wherein the substrate is a surface of an article.

**[Claim 16]** The method according to claim 14 wherein the substrate is a base coat layer applied to a surface of an article.

**[Claim 17]** The method according to claim 14 wherein the marking material comprises an infrared reflective inorganic pigment.

**[Claim 18]** The method according to claim 17 wherein the infrared reflective inorganic pigment is one or more selected from the group consisting of:

$\text{Mn}_2\text{V}_2\text{O}_7$ ;

$\text{M1}_x\text{MnO}_y$ , where M1 is calcium, strontium, barium, magnesium, yttrium and/or an element selected from the Lanthanide series of the Periodic Table of the Elements, x is a number from about 0.01 to about 99, and y is greater than or equal to  $X + 1$  and less than or equal to  $X + 2$  and designates the number of oxygen atoms required to maintain electroneutrality;

$\text{Bi}_2\text{Mn}_4\text{O}_{10}$ ; and

solid solutions having a corundum-hematite crystalline structure comprising iron oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, chrome, cobalt, gallium, indium, lanthanum, lithium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc; and

solid solutions having a corundum-hematite crystalline structure comprising chrome oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, cobalt, gallium, indium, iron, lanthanum, lithium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc.

**[Claim 19]** The method according to claim 14 wherein the average particle size of the inorganic pigment in the cover coating material is from about 0.02  $\mu\text{m}$  to about 15  $\mu\text{m}$ .

**[Claim 20]** The method according to claim 14 wherein the average particle size of the inorganic pigment in the cover coating material is from about 0.1  $\mu\text{m}$  to about 0.5  $\mu\text{m}$ .

**[Claim 21]** The method according to claim 14 wherein the substrate is selected from the group consisting of metal, glass, wood, plastic and ceramic.

**[Claim 22]** The method according to claim 14 wherein the marking material is selected from the group consisting of paint, enamel, laser marking composition, glass, ink, and transfer films.

**[Claim 23]** The method according to claim 14 wherein the cover coating material is selected from the group consisting of paint, glass, enamel, ink, and transfer films.

**[Claim 24]** The method according to claim 14 wherein the mark is in the form of a barcode.

**[Claim 25]** The method according to claim 14 wherein the inorganic pigment in the cover coating material is doped with one or more elements such that the inorganic pigment provides a uniquely identifiable spectral curve.

**[Claim 26]** The method according to claim 14 wherein the cover coating material comprises two or more different inorganic pigments that together provide a uniquely identifiable spectral curve.

**[Claim 27]** The method according to claim 14 wherein the contrast marking material comprises an infrared reflective inorganic pigment.

**[Claim 28]** The method according to claim 27 wherein the infrared reflective inorganic pigment is one or more selected from the group consisting of:

$\text{Mn}_2\text{V}_2\text{O}_7$ ;

$\text{M1}_x\text{Mn}_y$ , where M1 is calcium, strontium, barium, magnesium, yttrium and/or an element selected from the Lanthanide series of the Periodic Table of the Elements, x is a number from about 0.01 to about 99, and y is greater than or equal to  $X + 1$  and less than or equal to  $X + 2$  and designates the number of oxygen atoms required to maintain electroneutrality;

$\text{Bi}_2\text{Mn}_4\text{O}_{10}$ ; and

solid solutions having a corundum-hematite crystalline structure comprising iron oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, chrome, cobalt, gallium, indium, lanthanum, lithium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc; and

solid solutions having a corundum-hematite crystalline structure comprising chrome oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, cobalt, gallium, indium, iron, lanthanum, lithium,

magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc.

**[Claim 29]** A method of forming a durable infrared detectable mark on a substrate comprising:

applying a marking material to the substrate to form a mark;  
applying a masking material over a least a portion of the mark and, optionally, over a portion of the substrate, to form a mask, wherein mark reflects or absorbs radiation at a predetermined wavelength within the range of from about 0.75  $\mu\text{m}$  to about 40  $\mu\text{m}$  at a sufficiently different level than the mask such that the mark can be discerned from the mask at the predetermined wavelength; and  
applying a cover coating material comprising an inorganic pigment over the mark and the mask to form a cover coat that appears substantially opaque in the visible portion of the electromagnetic spectrum but is sufficiently transmissive of radiation emitted at the predetermined wavelength that the mark can be discerned from the mask through the cover coat at the predetermined wavelength.

**[Claim 30]** The method according to claim 29 wherein the substrate is a surface of an article.

**[Claim 31]** The method according to claim 29 wherein the substrate is a base coat layer applied to a surface of an article.

**[Claim 32]** The method according to claim 29 wherein the marking material comprises an infrared reflective inorganic pigment.

**[Claim 33]** The method according to claim 32 wherein the infrared reflective inorganic pigment is one or more selected from the group consisting of:

$\text{Mn}_2\text{V}_2\text{O}_7$ ;

$\text{M1}_x\text{MnO}_y$ , where M1 is calcium, strontium, barium, magnesium, yttrium and/or an element selected from the Lanthanide series of the Periodic Table of the Elements, x is a number from about 0.01 to about 99, and y is greater than or equal to  $X + 1$  and less than or equal to  $X + 2$  and designates the number of oxygen atoms required to maintain electroneutrality;

$\text{Bi}_2\text{Mn}_4\text{O}_{10}$ ; and

solid solutions having a corundum-hematite crystalline structure comprising iron oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, chrome, cobalt, gallium, indium, lanthanum, lithium,

magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc; and

solid solutions having a corundum-hematite crystalline structure comprising chrome oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, cobalt, gallium, indium, iron, lanthanum, lithium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc.

**[Claim 34]** The method according to claim 29 wherein the average particle size of the inorganic pigment in the cover coating material is from about 0.02  $\mu\text{m}$  to about 15  $\mu\text{m}$ .

**[Claim 35]** The method according to claim 29 wherein the average particle size of the inorganic pigment in the cover coating material is from about 0.1  $\mu\text{m}$  to about 0.5  $\mu\text{m}$ .

**[Claim 36]** The method according to claim 29 wherein the substrate is selected from the group consisting of metal, glass, wood, plastic and ceramic.

**[Claim 37]** The method according to claim 29 wherein the marking material is selected from the group consisting of paint, enamel, laser marking composition, glass, ink, and transfer films.

**[Claim 38]** The method according to claim 29 wherein the cover coating material is selected from the group consisting of paint, glass, enamel, ink, and transfer films.

**[Claim 39]** The method according to claim 29 wherein the mark is in the form of a bar code.

**[Claim 40]** The method according to claim 29 wherein the inorganic pigment in the cover coating material is doped with one or more elements such that the inorganic pigment provides a uniquely identifiable spectral curve.

**[Claim 41]** The method according to claim 29 wherein the cover coating material comprises two or more different inorganic pigments that together provide a uniquely identifiable spectral curve.

**[Claim 42]** The method according to claim 29 wherein the masking material comprises an infrared reflective inorganic pigment.

**[Claim 43]** The method according to claim 42 wherein the infrared reflective inorganic pigment is one or more selected from the group consisting of:

$\text{Mn}_2\text{V}_2\text{O}_7$ ;

$\text{M}_1\text{xMnO}_y$ , where  $\text{M}_1$  is calcium, strontium, barium, magnesium, yttrium and/or an element selected from the Lanthanide series of the Periodic Table of the Elements,  $\text{x}$  is a number from about 0.01 to about 99, and  $\text{y}$  is greater than or

equal to  $X + 1$  and less than or equal to  $X + 2$  and designates the number of oxygen atoms required to maintain electroneutrality;

$\text{Bi}_2\text{Mn}_4\text{O}_{10}$ ; and

solid solutions having a corundum-hematite crystalline structure comprising iron oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, chrome, cobalt, gallium, indium, lanthanum, lithium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc; and

solid solutions having a corundum-hematite crystalline structure comprising chrome oxide a host component doped with guest elements selected from aluminum, antimony, bismuth, boron, cobalt, gallium, indium, iron, lanthanum, lithium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium and zinc.

**[Claim 44]** A multilayer coating comprising a marking layer disposed between a substrate and a cover coating layer that comprises an inorganic pigment, wherein the marking layer reflects or absorbs radiation at a predetermined wavelength within the range of from about 0.75  $\mu\text{m}$  to about 40  $\mu\text{m}$  at a sufficiently different level than the substrate, and wherein the cover coating layer appears substantially opaque in the visible portion of the electromagnetic spectrum but is sufficiently transmissive of radiation emitted at the predetermined wavelength that the mark can be discerned from the substrate through the cover coat at the predetermined wavelength.

**[Claim 45]** An article marked with a non-visible authentication mark comprising a marking layer disposed between a surface of the article and a cover coating layer that comprises an inorganic pigment, wherein the marking layer reflects or absorbs radiation at a predetermined wavelength within the range of from about 0.75  $\mu\text{m}$  to about 40  $\mu\text{m}$  at a sufficiently different level than an area beneath the cover coating adjacent to the marking layer, and wherein the cover coating layer appears substantially opaque in the visible portion of the electromagnetic spectrum but is sufficiently transmissive of radiation emitted at the predetermined wavelength that the mark can be discerned from the area beneath the cover coating adjacent to the marking layer through the cover coat at the predetermined wavelength.